



(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
06.04.2005 Bulletin 2005/14

(51) Int Cl.7: **G11C 13/02**, H01L 51/30,  
**G11C 16/04**

(21) Application number: **03257104.4**

(22) Date of filing: **11.11.2003**

(54) **Nonvolatile memory device utilising vertical nanotube**

Nichtflüchtige Speichervorrichtung mit vertikalen Nanoröhren

Dispositif de mémoire non volatile utilisant des nanotubes verticaux

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **15.11.2002 KR 2002071041**

(43) Date of publication of application:  
**19.05.2004 Bulletin 2004/21**

(73) Proprietor: **SAMSUNG ELECTRONICS CO., LTD.**  
**Suwon-City, Kyungki-do (KR)**

(72) Inventors:  
• **Choi, Won-bong**  
**Suwon-city Kyungki-do (KR)**

- **Lee, Jo-won**  
**Suwon-city Kyungki-do (KR)**
- **Kang, Ho-kyu, 503-1002 Jinsan Maeul**  
**Yongin-city Kyungki-do (KR)**
- **Kim, Chung-woo, 101-705 Park Town Daelim Apt.**  
**Seongnam-city Kyungki-do (KR)**

(74) Representative: **Greene, Simon Kenneth**  
**Elkington and Fife LLP,**  
**Prospect House,**  
**8 Pembroke Road**  
**Sevenoaks, Kent TN13 1XR (GB)**

(56) References cited:  
**WO-A-00/48195** **US-B1- 6 313 503**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

[0001] The present invention relates to a memory device, and more particularly, to a high-density memory device using a carbon nanotube as a vertical electron transport channel.

[0002] Memory devices using a semiconductor generally include a transistor, which serves as a switch for forming a current path when information is written to or read from a capacitor, and a capacitor, which stores and preserves electrical charges. In order to make a current flow of large intensity in the transistor, the transistor needs to have a high transconductance (gm) characteristic. Accordingly, a conventional Metal Oxide Field Effect Transistor (MOSFET) having a high transconductance characteristic has been lately used as a switching device for a semiconductor memory device.

[0003] The conventional MOSFET mainly includes a control gate formed of doped polycrystalline silicon and a source and drain region formed of doped crystalline silicon. Under the same voltage condition, the transconductance of the MOSFET is inversely proportional to a channel length and the thickness of a gate oxide layer but is proportional to a surface mobility, a dielectric constant of the gate oxide layer, and a channel width. Since the surface mobility and the dielectric constant of an oxide layer are predetermined according to materials, such as a silicon wafer with an orientation and a silicon oxide layer, a high transconductance can be accomplished by increasing a ratio of the channel width to the channel length or decreasing the thickness of the oxide layer.

[0004] However, the physical size of the conventional MOSFET needs to be reduced in order to manufacture a high-density memory device, so the size of the gate and the size of the source and drain region also need to be reduced, which causes various problems.

[0005] For example, when the size of a control gate is reduced, a cross section of the control gate is reduced, which induces a large electrical resistance in a transistor. Reduction of the source and drain region causes the thickness, i.e., junction depth, to be reduced, and therefore, a large electrical resistance is induced or a punch through phenomenon, in which a depletion layer of a source contacts a depletion layer of a drain due to a decrease in a distance between the source and the drain, occurs. Consequently, it is impossible to control a current flow. In addition, size reduction of such a memory device decreases the width of a channel functioning as a current path below 30 nm, and therefore, the flow of current is disturbed. As a result, the memory device operates abnormally. In other words, the use of the conventional silicon MOSFET is limited in accomplishing a high density memory device.

[0006] According to an aspect of the present invention, there is provided a memory device including a substrate having a source region; a nanotube array, which is composed of a plurality of nanotube columns which

are vertically grown on the substrate such that one end of the nanotube array is in contact with the source region, thereby functioning as an electron transport channel; a memory cell, which is formed around an outer side surface of the nanotube array; a control gate, which is formed around an outer side surface of the memory cell; and a drain region, which is in contact with the other end of the nanotube array.

[0007] The present invention provides a high-density memory device which prevents a resistance from increasing due to miniaturization and reduces the risk of an abnormal operation by using a nanotube.

[0008] Preferably, the substrate is made of aluminum oxide, silicon, or a mesoporous material.

[0009] Preferably, the plurality of nanotube columns are made of carbon, boronitride, or gallium phosphate.

[0010] Preferably, the memory cell includes a first insulation layer formed around the outer side surface of the nanotube array; an electron storing layer formed around an outer side surface of the first insulation layer; and a second insulation layer formed around an outer side surface of the electron storing layer to be in contact with the control gate.

[0011] Preferably, the first and second insulation layers are silicon oxide layers.

[0012] Preferably, the electron storing layer is a silicon layer or a silicon nitride layer.

[0013] Preferably, the electron storing layer has a thickness of 100 nm or less, and the electron storing layer is a porous layer including a plurality of nanodots filled with an electron storing material.

[0014] Preferably, the electron storing material is silicon or silicon nitride.

[0015] Preferably, the porous layer is an aluminum oxide layer.

[0016] Preferably, the nanodots have a diameter of 100 nm or less.

[0017] The present invention provides a high-density and large capacity memory device by utilizing a nanotube as an electron transport channel and vertically arranging a plurality of nanotube columns.

[0018] The above and other features and advantages of the present invention will become more apparent by describing in detail preferred embodiments thereof with reference to the attached drawings in which:

FIG. 1A is a cross section of a memory device according to a first embodiment of the present invention;

FIG. 1B is a perspective view of a memory device according to the first embodiment of the present invention;

FIG. 2 is a cross section of a memory device according to a second embodiment of the present invention;

FIG. 3 is a photograph of carbon nanotubes grown on a substrate in order to manufacture a memory device according to the first embodiment of the

present invention; and

FIG. 4 is a graph showing current-voltage (I-V) characteristics of a memory device according to the first embodiment of the present invention.

[0019] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the attached drawings.

[0020] FIGS. 1A and 1B are a cross section and a perspective view, respectively, of a memory device according to a first embodiment of the present invention. Referring to FIGS. 1A and 1B, a substrate 11 includes a source region (S) 13. A nanotube column 10 is vertically positioned on a top surface of the substrate 11 to be connected to the source region 13. A memory cell 19 is formed around an outer surface of the nanotube column 10. A control gate (G) 17 is formed around an outer surface of the memory cell 19. A drain region (D) 15 is formed on a top surface of the nanotube column 10 and the memory cell 19. A plurality of memory devices having this structure may form an array on the substrate 11.

[0021] It is preferable that the substrate 11 is made of aluminum oxide ( $\text{Al}_2\text{O}_3$ ), silicon (Si), or mesoporous material. The source region 13 is formed by doping the substrate 11 with ions.

[0022] The nanotube column 10 can be formed using a semiconductor nanotube such as a carbon nanotube, a boronitride (BN) nanotube, or a gallium phosphate nanotube. Nanotubes are divided into metal nanotubes and semiconductor nanotubes according to electrical characteristics. Metal nanotubes are not influenced by a gate voltage and have linear current-voltage characteristics, and semiconductor nanotubes are influenced by a gate voltage and have non-linear current-voltage characteristics. A memory device according to the present invention uses semiconductor nanotubes so that the flow of electrons, i.e., current, moving through the nanotube columns 10 is controlled according to a gate voltage applied to the control gate 17.

[0023] Here, carbon nanotubes utilized as nanotube columns 10 are grown on the substrate 11 using arc discharge, laser vaporization, plasma enhanced chemical vapor deposition (PECVD), thermal chemical vapor deposition, or a vapor phase growth such that one end of each carbon nanotube columns 10 is in contact with the source region 13.

[0024] The memory cell 19 formed around the outer side surface of the nanotube column 10 may be made of an oxide-nitride-oxide (ONO) layer, in which oxide layers 19a and 19c function as insulation layers and a nitride layer 19b functions as an electron storing layer. The ONO layer may be formed using chemical vapor deposition (CVD) or heat treatment. The nitride layer 19b may be made of silicon nitride ( $\text{Si}_3\text{N}_4$ ). Instead of a nitride layer, a silicon layer may be used. It is preferable that the thickness of the memory cell 19 is less than 200 nm and the thickness of the nitride layer 19b is 100 nm or less.

[0025] The control gate 17 is formed around the outer side surface of the memory cell 19. The drain region 15 is formed on the top surface of the nanotube column 10 and the memory cell 19 to be in contact with the other end of the nanotube column 10.

[0026] FIG. 2 is a cross section of a memory device according to a second embodiment of the present invention. The memory device shown in FIG. 2 has the same structure as the memory device according to the first embodiment shown in FIGS. 1A and 1B, with the exception that a memory cell 29 includes a porous layer 29b containing a nanodot 28 filled with an electron storing material. Reference numerals 29a and 29c denotes layers having the same functions as the oxide layers 19a and 19c, respectively, shown in FIGS. 1A and 1B.

[0027] When the porous layer 29b is formed, an electric power is applied to an aluminum substrate placed in a sulphuric acid solution or a phosphoric acid solution so as to anodize the aluminum substrate, thereby forming a plurality of nanodots 28. Then, the nanodots 28 are filled with an electron storing material such as silicon or silicon nitride using CVD or sputtering. Thus, the porous layer 29b functions as an electron storing layer.

[0028] FIG. 3 is a photograph of carbon nanotubes grown on a substrate in order to manufacture a memory device according to the first embodiment of the present invention.

[0029] FIG. 4 is a graph showing current-voltage (I-V) characteristics of a memory device according to the first embodiment of the present invention. Referring to FIG. 4, a drain current  $I_d$  is maintained constant until a gate voltage increases from a negative value to 0 and then remarkably decreases when the gate voltage increases above 0. In other words, the memory device according to the first embodiment of the present invention clearly shows the operating characteristics of a high density memory device.

[0030] According to the present invention, an ultrahigh density memory device can be implemented using nanotubes. Since the ultrahigh density memory device can be structured on a substrate without performing a doping process by using self-assembly when the present invention is implemented, manufacturing processes therefor can be simplified.

[0031] While this invention has been particularly shown and described with reference to preferred embodiments thereof, the preferred embodiments should be considered in descriptive senses only and not for purposes of limitation. For example, other materials having an excellent ability to capture electrons can be used as an electron storing layer or material. Therefore, the scope of the invention is defined not by the detailed description of the invention but by the appended claims.

## Claims

1. A memory device comprising:

a substrate having a source region;  
 a nanotube array, which is composed of a plurality of nanotube columns which are vertically arranged on the substrate such that one end of the nanotube array is in contact with the source region, thereby functioning as an electron transport channel;  
 a memory cell, which is formed around an outer side surface of the nanotube array;  
 a control gate, which is formed around an outer side surface of the memory cell; and  
 a drain region, which is in contact with the other end of the nanotube array.

2. The memory device of claim 1, wherein the substrate is made of one selected from the group consisting of aluminum oxide, silicon, and a mesoporous material.
3. The memory device of claim 1 or 2, wherein the plurality of nanotube columns are made of one selected from the group consisting of carbon, boronitride, and gallium phosphate.
4. The memory device of any preceding claim, wherein the memory cell comprises:
  - a first insulation layer formed around the outer side surface of the nanotube array;
  - an electron storing layer formed around an outer side surface of the first insulation layer; and
  - a second insulation layer formed around an outer side surface of the electron storing layer to be in contact with the control gate.
5. The memory device of claim 4, wherein the first and second insulation layers are silicon oxide layers.
6. The memory device of claim 4 or 5, wherein the electron storing layer is one of a silicon layer and a silicon nitride layer.
7. The memory device of claim 4, 5 or 6, wherein the electron storing layer has a thickness of 100 nm or less.
8. The memory device of claim 4, 5, 6 or 7, wherein the electron storing layer is a porous layer comprising a plurality of nanodots filled with an electron storing material.
9. The memory device of claim 8, wherein the electron storing material is one of silicon and silicon nitride.
10. The memory device of claim 8 or 9, wherein the porous layer is an aluminum oxide layer.
11. The memory device of claims 5 through 10, wherein

the nanodots have a diameter of 100 nm or less.

## Patentansprüche

### 1. Speichervorrichtung umfassend:

ein Substrat mit einem Sourcebereich;  
 eine Nanoröhrenanordnung, die aus einer Mehrzahl von Nanoröhrensäulen gebildet ist, die vertikal auf dem Substrat derart angeordnet sind, dass ein Ende der Nanoröhrenanordnung mit dem Sourcebereich in Kontakt steht, wodurch sie als Elektronentransportkanal funktioniert;  
 eine Speicherzelle, die um eine Außenseitenfläche der Nanoröhrenanordnung gebildet ist;  
 ein Steuergate, das um eine Außenseitenfläche der Speicherzelle gebildet ist; und  
 einen Drainbereich, der mit dem anderen Ende der Nanoröhrenanordnung in Kontakt steht.

### 2. Speichervorrichtung nach Anspruch 1, worin das Substrat aus einem ausgewählt aus der Gruppe bestehend aus Aluminiumoxid, Silicium und einem mesoporösen Material gebildet ist.

### 3. Speichervorrichtung nach Anspruch 1 oder 2, worin die Mehrzahl von Nanoröhrensäulen aus einem ausgewählt aus der Gruppe bestehend aus Kohlenstoff, Bornitrid und Galliumphosphat gebildet ist.

### 4. Speichervorrichtung nach einem der vorhergehenden Ansprüche, worin die Speicherzelle umfasst:

eine erste Isolierschicht gebildet um die Außenseitenfläche der Nanoröhrenanordnung;  
 eine Elektronenspeicherschicht gebildet um eine Außenseitenfläche der ersten Isolierschicht; und  
 eine zweite Isolierschicht gebildet um eine Außenseitenfläche der Elektronenspeicherschicht, so dass sie mit dem Steuergate in Kontakt steht.

### 5. Speichervorrichtung nach Anspruch 4, worin die erste und zweite Isolierschicht Siliciumoxidschichten sind.

### 6. Speichervorrichtung nach Anspruch 4 oder 5, worin die Elektronenspeicherschicht eine Siliciumschicht oder eine Siliciumnitridschicht ist.

### 7. Speichervorrichtung nach Anspruch 4, 5 oder 6, worin die Elektronenspeicherschicht eine Dicke von 100 nm oder weniger aufweist.

### 8. Speichervorrichtung nach Anspruch 4, 5, 6 oder 7,

worin die Elektronenspeicherschicht eine poröse Schicht ist, die eine Mehrzahl von Nanodots gefüllt mit einem Elektronenspeichermaterial umfasst.

9. Speichervorrichtung nach Anspruch 8, worin das Elektronenspeichermaterial Silicium oder Siliciumnitrid ist. 5
10. Speichervorrichtung nach Anspruch 8 oder 9, worin die poröse Schicht eine Aluminiumoxidschicht ist. 10
11. Speichervorrichtung nach den Ansprüchen 5 bis 10, worin die Nanodots einen Durchmesser von 100 nm oder weniger aufweisen. 15

#### Revendications

1. Dispositif de mémoire comprenant :

un matériau de base possédant une région de source ;  
 un ensemble de nanotube, composé d'une pluralité de colonnes de nanotube disposées verticalement sur le matériau de base de telle manière qu'une extrémité de l'ensemble de nanotube soit en contact avec la région de source, fonctionnant ainsi comme un canal de transport d'électrons ;  
 une cellule de mémoire, formée autour d'une surface du côté externe de l'ensemble de nanotube ;  
 une porte de commande, formée autour d'une surface du côté externe de la cellule de mémoire ; et  
 une région de drain, en contact avec l'autre extrémité de l'ensemble de nanotube.

2. Dispositif de mémoire selon la revendication 1, dans lequel le matériau de base est composé de l'élément choisi dans le groupe comprenant de l'alumine, du silicium, et un matériau mésoporeux. 40
3. Dispositif de mémoire selon la revendication 1 ou 2, dans lequel la pluralité de colonnes de nanotube sont composées d'un élément choisi dans le groupe comprenant du carbone, du boronitride, et du phosphate de gallium. 45
4. Dispositif de mémoire selon l'une quelconque des revendications précédentes, dans lequel la cellule de mémoire comprend :

une première couche d'isolement formée autour de la surface du côté externe de l'ensemble de nanotube ;  
 une couche de stockage d'électrons formée autour d'une surface du côté externe de la pre-

mière couche d'isolement ; et  
 une seconde couche d'isolement formée autour d'une surface du côté externe de la couche de stockage d'électrons offrant un contact avec la porte de commande.

5. Dispositif de mémoire selon la revendication 4, dans lequel la première et la seconde couches d'isolement sont des couches d'oxyde de silicium.
6. Dispositif de mémoire selon la revendication 4 ou 5, dans lequel la couche de stockage d'électrons est composée d'une couche de silicium et d'une couche de nitrure de silicium.
7. Dispositif de mémoire selon la revendication 4, 5 ou 6, dans lequel la couche de stockage d'électrons possède une épaisseur de 100 nm ou moins.
8. Dispositif de mémoire selon la revendication 4, 5, 6 ou 7, dans lequel la couche de stockage d'électrons est une couche poreuse comprenant une pluralité de nanopoints remplis d'un matériau de stockage d'électrons.
9. Dispositif de mémoire selon la revendication 8, dans lequel le matériau de stockage d'électrons est composé de silicium et de nitrure de silicium.
10. Dispositif de mémoire selon la revendication 8 ou 9, dans lequel la couche poreuse est une couche d'oxyde d'aluminium.
11. Dispositif de mémoire selon les revendications 5 à 10, dans lequel les nanopoints possèdent un diamètre de 100 nm ou moins.

FIG. 1A

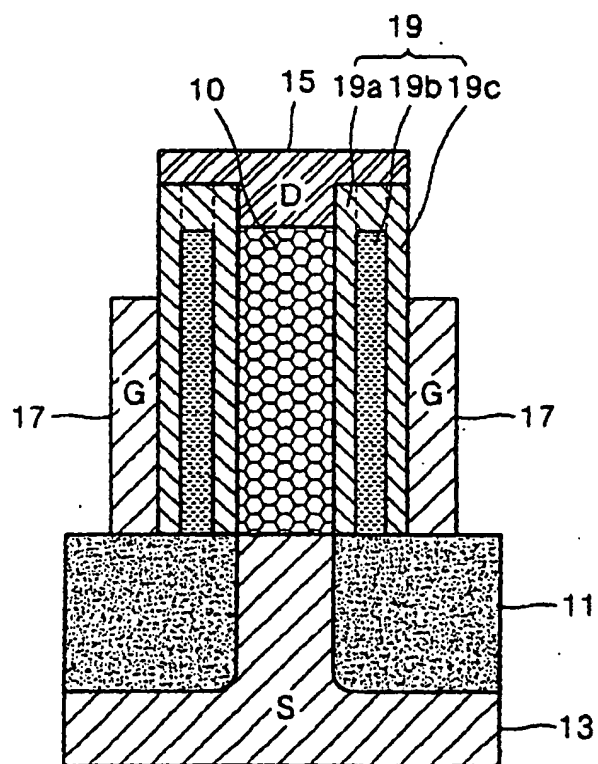


FIG. 1B

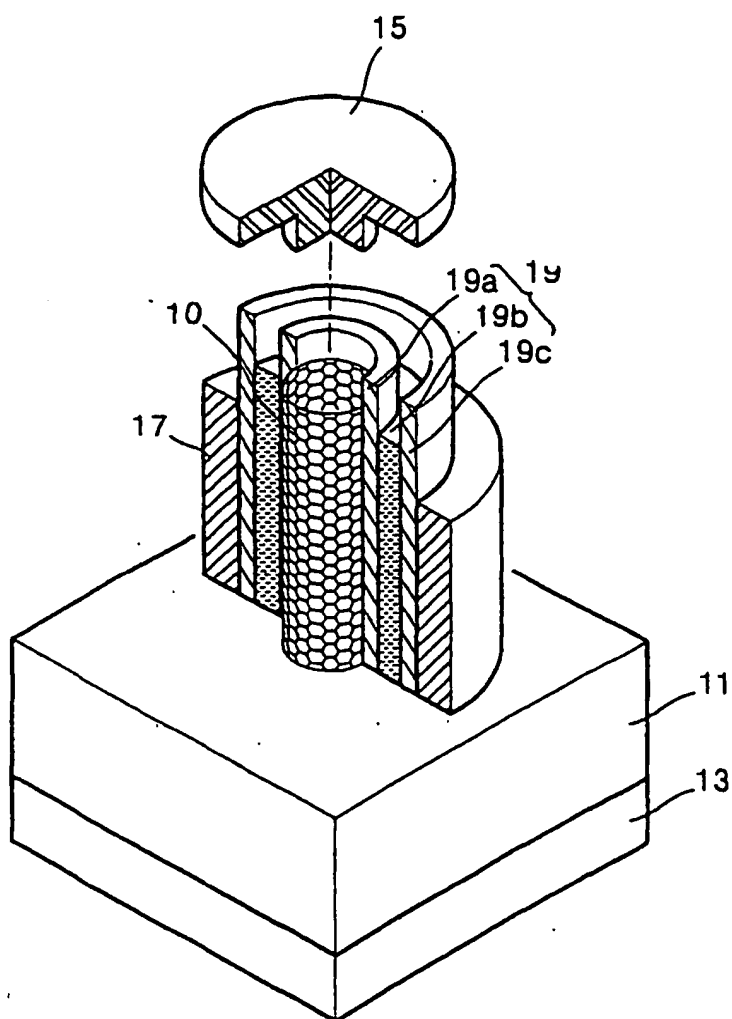


FIG. 2

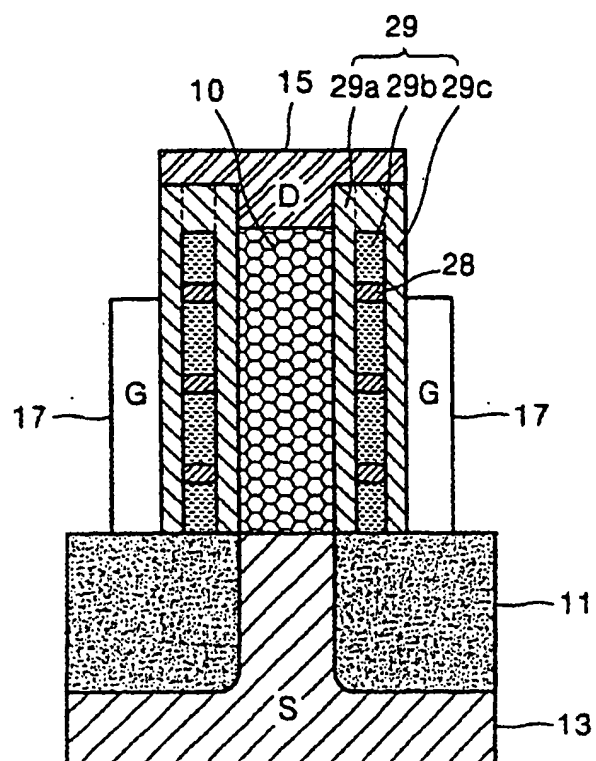


FIG. 3

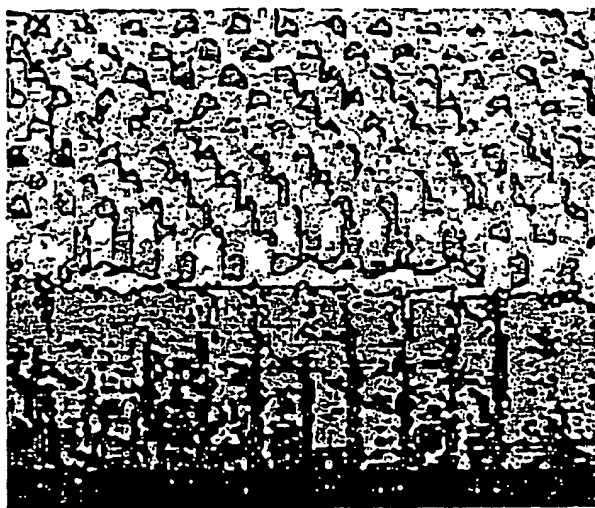


FIG. 4

